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Self-Interaction Free and Analytic Treatment of the Coulomb Energy in Kohn-Sham Density Functional Theory

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Overview

- The use of the classical Hartree term in implementations of KS-DFT leads to self-interaction effects.

- A great number of functionals has been developed over the years with the purpose of removing the effects of self- interaction from the theory.

- We have now solved uniquely, analytically and in closed form the self-interaction problem in Kohn-Sham Density Functional Theory.

- We will describe how this is done, and show results of calculations for realistic atomic systems and will compare with competing methodologies (OEP, exact exchange).

- **The underlying formalism is that of Density Function Theory(DFT), in which <u>the independent variable is the density n(r)</u>.**

- **Functional derivatives taken only with respect to the density**

Kohn-Sham Density Functional Theory

<u>real system</u>

<u>fictitious non-interacting system with the same density</u>

$$\hat{H} = V_{ext} + \hat{T} + \hat{U}$$

$$E[n] = \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$$

$$\hat{H}_s = V_s + \hat{T}$$

$$E_s[n] = \langle \Phi | V_s + \hat{T} | \Phi \rangle$$

$$= \int V_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Phi | \hat{T} | \Phi \rangle$$

Hohenberg and Kohn have shown that

$$\left. \frac{\delta E[n]}{\delta n(\mathbf{r})} \right|_{n=n_{GS}} = 0$$

$$\left. \frac{\delta E_s[n]}{\delta n(\mathbf{r})} \right|_{n=n_{GS}} = 0$$

$$\left. \frac{\delta \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle}{\delta n(\mathbf{r})} \right|_{n=n_{GS}, \Psi=\Psi_{GS}} = -V_{ext}$$

$$\left. \frac{\delta \langle \Phi | \hat{T} | \Phi \rangle}{\delta n(\mathbf{r})} \right|_{n=n_{GS}, \Phi=\Phi_{GS}} = -V_s$$

$$\langle \Psi_{GS} | \hat{T} + \hat{U} | \Psi_{GS} \rangle \leq \langle \Phi_{GS} | \hat{T} + \hat{U} | \Phi_{GS} \rangle$$

Kohn-Sham Density Functional Theory

$$V_s(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta}{\delta n(\mathbf{r})} \langle \Phi_{GS} | \hat{U} | \Phi_{GS} \rangle + \frac{\delta E_c[n]}{\delta n(\mathbf{r})}$$

Kohn-Sham equations $\left[\hat{T} + V_s \right] f_i = \varepsilon_i f_i$

Φ is a Slater Determinant build of f_i

pair density

$$U = \frac{1}{2} \int \int \frac{n^{(2)}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \int \int \frac{J(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

exchange term: $J(\mathbf{r}, \mathbf{r}') = -\sum_{ij} f_i^*(\mathbf{r}) f_j^*(\mathbf{r}') f_j(\mathbf{r}) f_i(\mathbf{r}') \delta_{\sigma_i, \sigma_j}$

The exchange term depends only implicitly on the density!

New Method of Calculating the Functional Derivative

- expand orbitals in orthonormal and complete basis

- basis written explicitly in term of the density

- differentiate the expansion (functional differentiation)

- get the potential

Equidensity Basis

new basis as functional of n:
$$\phi_{\mathbf{k}}(\mathbf{r},[n]) = \sqrt{\frac{n(\mathbf{r})}{N}} \exp\{i\mathbf{k}\cdot\mathbf{R}(\mathbf{r},[n])\}$$

John E. Harriman, Phys. Rev. **A** 24, 680 (1981)
Gil Zumbach and Klaus Maschke, Phys. Rev. A **2**, 544 (1983)

with

$\boldsymbol{k}=(k_x, k_y, k_z)$

$$R_1(\mathbf{r}) = R_1(x,y,z) = 2\pi \frac{\int_{-\infty}^{x} dx'\, n(x',y,z)}{\int_{-\infty}^{\infty} dx'\, n(x',y,z)}$$

$$R_2(\mathbf{r}) = R_2(y,z) = 2\pi \frac{\int_{-\infty}^{y} dy' \int_{-\infty}^{\infty} dx'\, n(x',y',z)}{\int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx'\, n(x',y',z)}$$

$$R_3(\mathbf{r}) = R_3(z) = \frac{2\pi}{N} \int_{-\infty}^{z} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx'\, n(x',y',z')$$
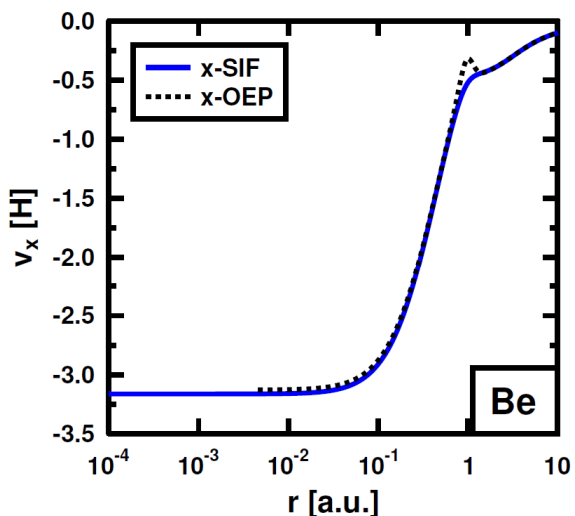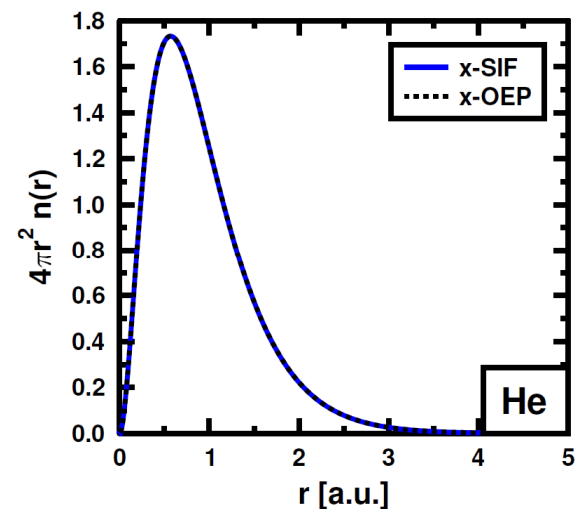
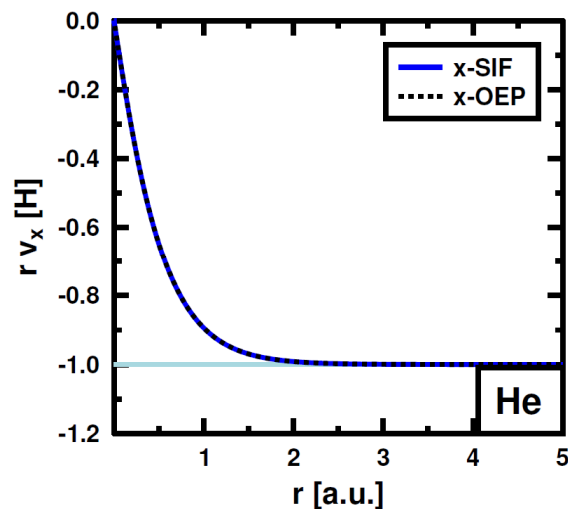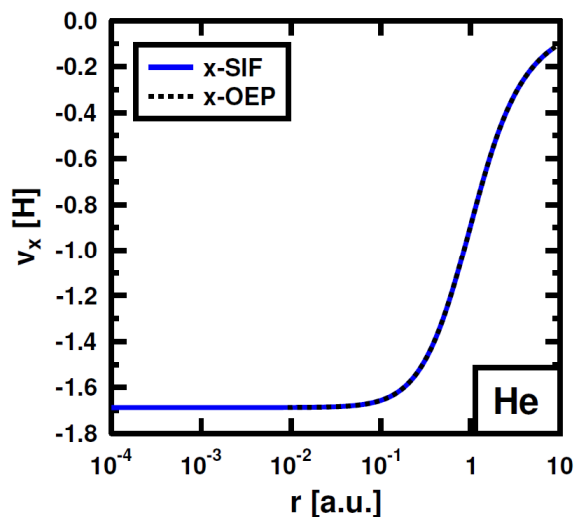The equidensity basis is complete and orthonormal (in **r**) for any density !!!

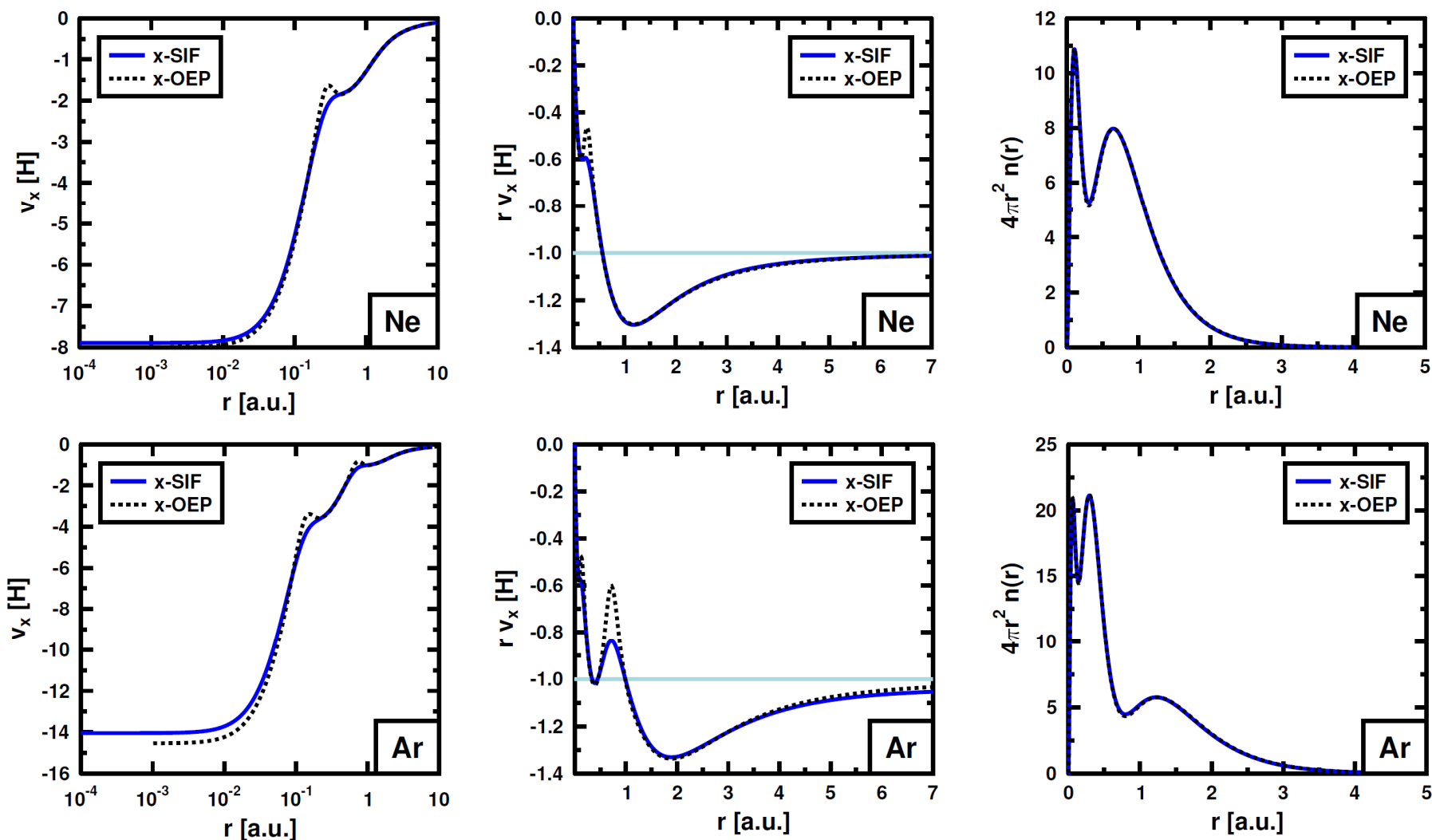a representation of orbitals in this basis is possible

$$f_j(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}}^{j}\, \phi_{\mathbf{k}}(\mathbf{r},[n])$$

$$\frac{\delta f_i(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta \mathbf{R}[n(\mathbf{r})]}{\delta n(\mathbf{r}')} \cdot \sum_{\mathbf{k}} a_{\mathbf{k}}^{i}\, i\mathbf{k}\, \phi_{\mathbf{k}}[n(\mathbf{r})] + \frac{\delta(\mathbf{r}-\mathbf{r}')}{2n(\mathbf{r})}\, f_i(\mathbf{r})$$
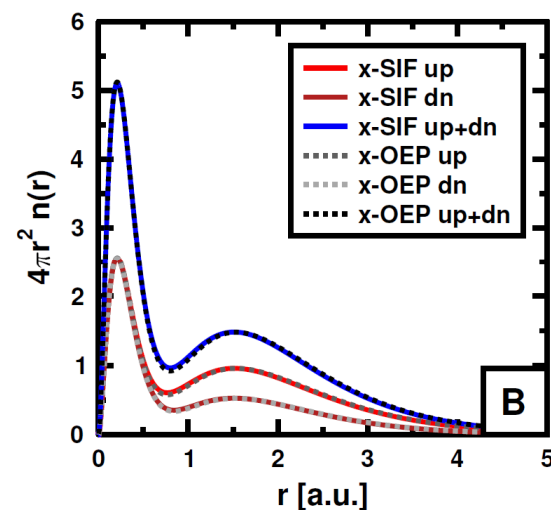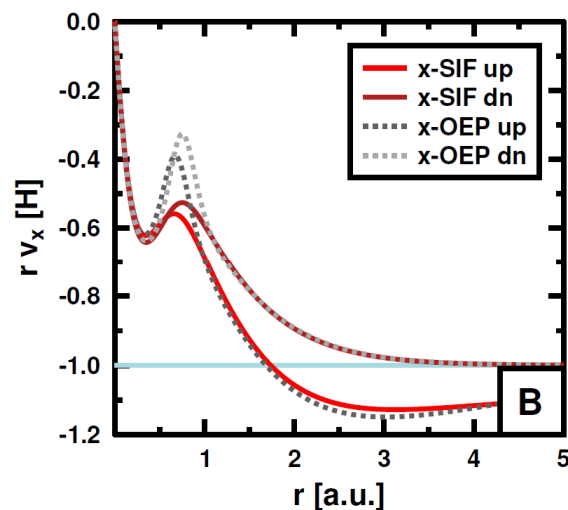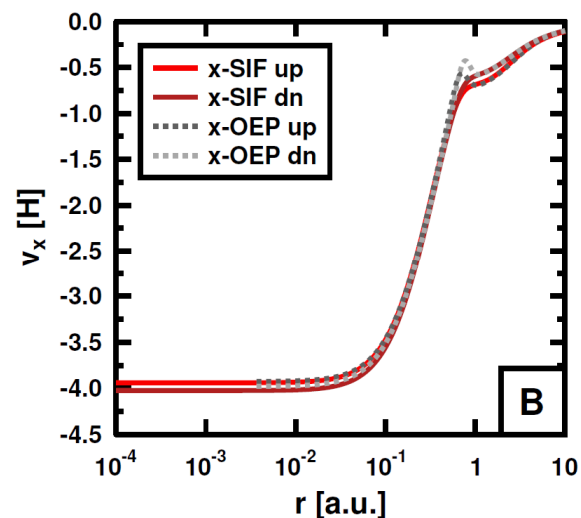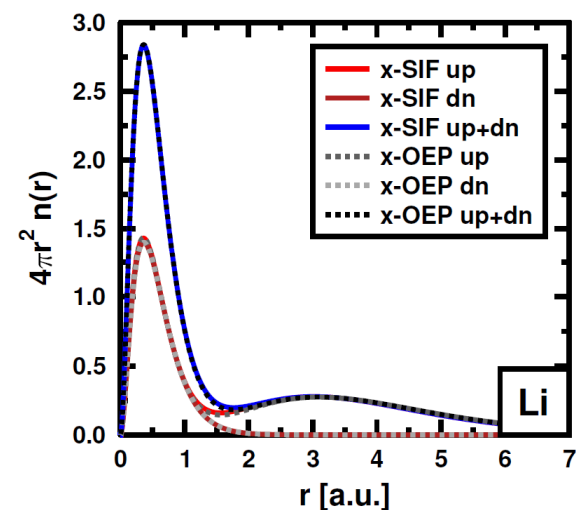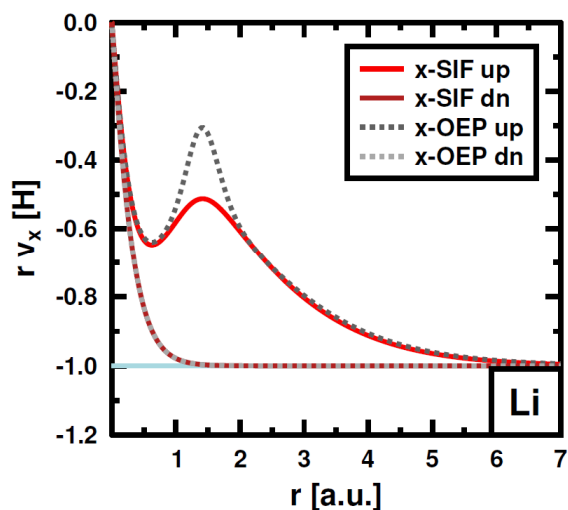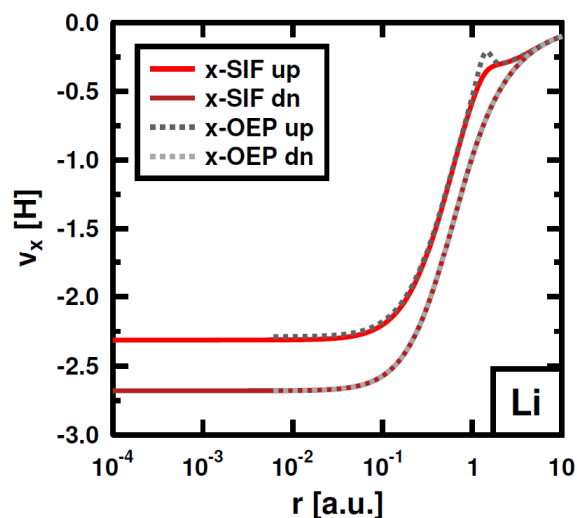
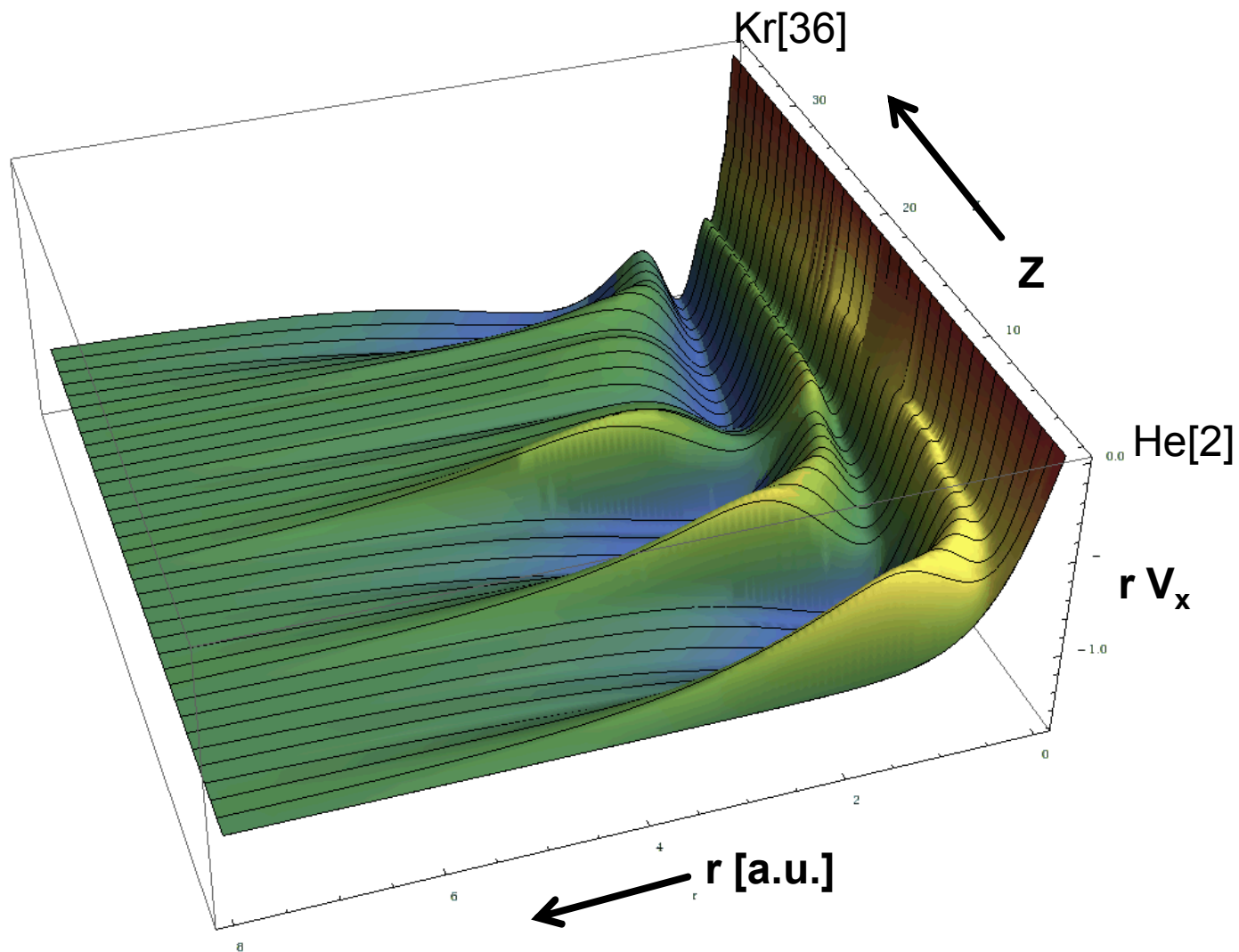# Exchange Potential: He and Be
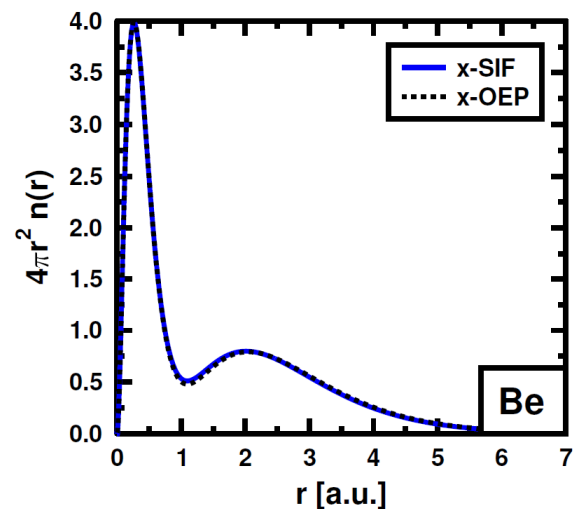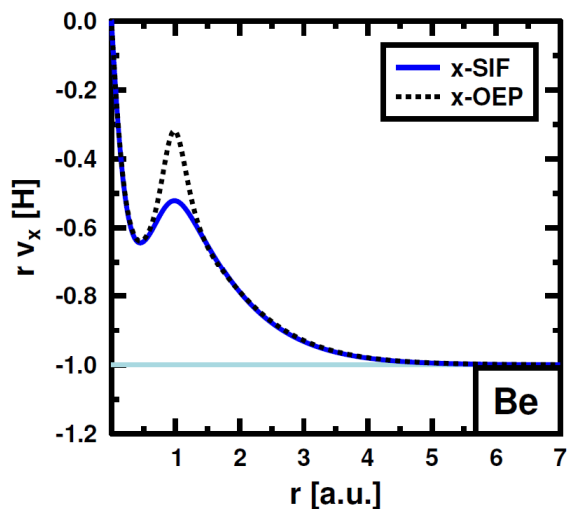
Exchange Potential: Ne and Ar

Exchange Potential: Li and B

Exchange Potential: He to Kr

Energies – Atom Series

Z	Symbol	Name	Exp	x-SIF	x-OEP	HF
2	He	Helium	-2.904	-2.862	-2.862	-2.862
3	Li	Lithium	-7.47806	-7.432	-7.433	-7.433
4	Be	Beryllium	-14.66736	-14.571	-14.572	-14.573
5	B	Boron	-24.65391	-24.527	-24.528	-24.529
6	C	Carbon	-37.8450	-37.687	-37.689	-37.690
7	N	Nitrogen	-54.5892	-54.401	-54.403	-54.405
8	O	Oxygen	-75.0673	-74.809	-74.812	-74.814
9	F	Fluorine	-99.7339	-99.406	-99.409	-99.411
10	Ne	Neon	-128.9376	-128.542	-128.545	-128.547
11	Na	Sodium	-162.2546	-161.852	-161.857	-161.859
12	Mg	Magnesium	-200.053	-199.606	-199.612	-199.615
13	Al	Aluminum	-242.346	-241.868	-241.873	-241.877
14	Si	Silicon	-289.359	-288.845	-288.851	-288.854
15	P	Phosphorus	-341.259	-340.709	-340.715	-340.719
16	S	Sulfur	-398.110	-397.495	-397.502	-397.506
17	Cl	Chlorine	-460.148	-459.470	-459.478	-459.483
18	Ar	Argon	-527.540	-526.804	-526.812	-526.817

energies in H

we find: $E_g \leq E^{HF} \leq E^{OEP} \leq E^{SIF}$

Energies – Atom Series
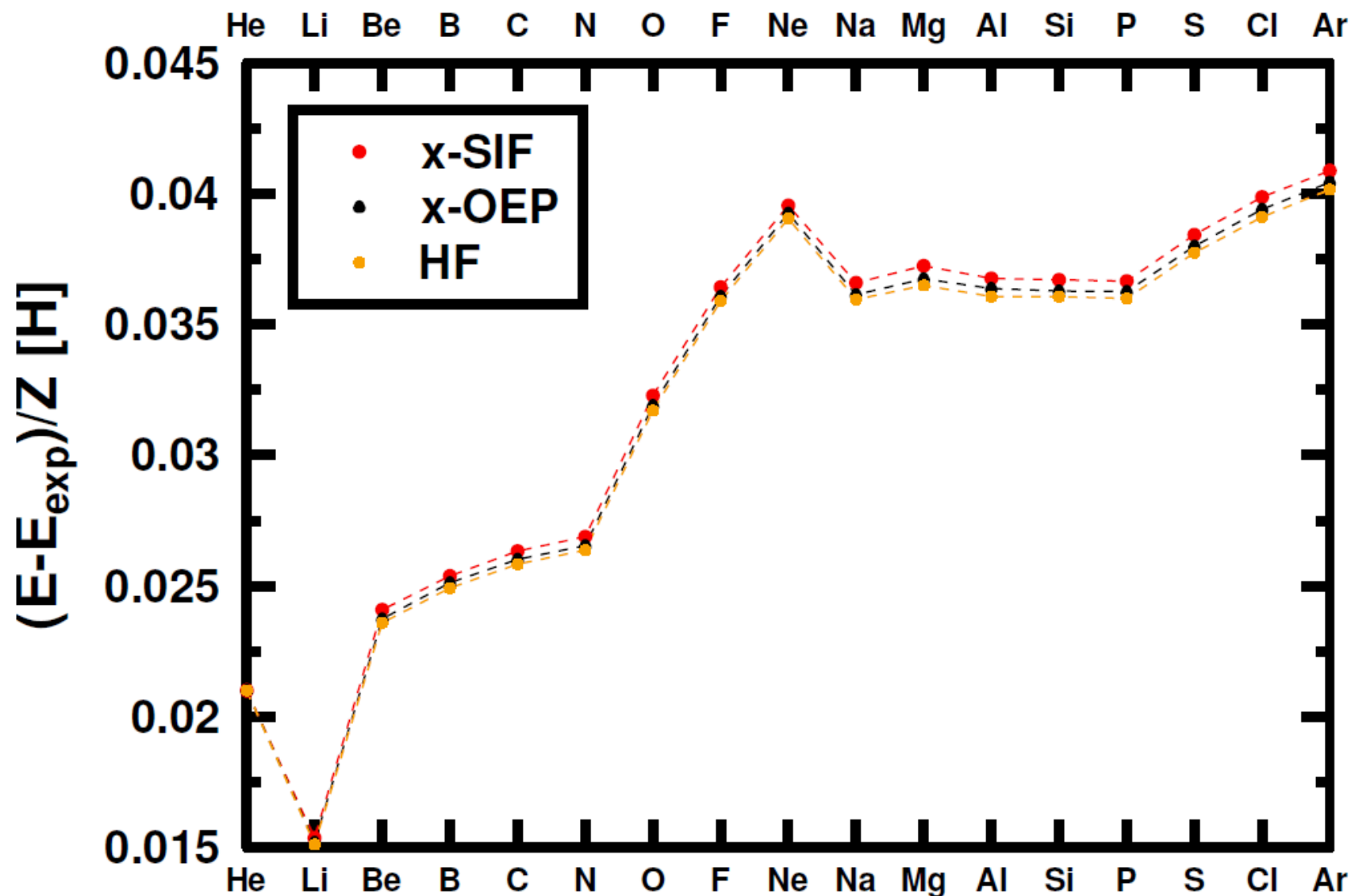
Comparison to OEP

DFT condition for the ground state:
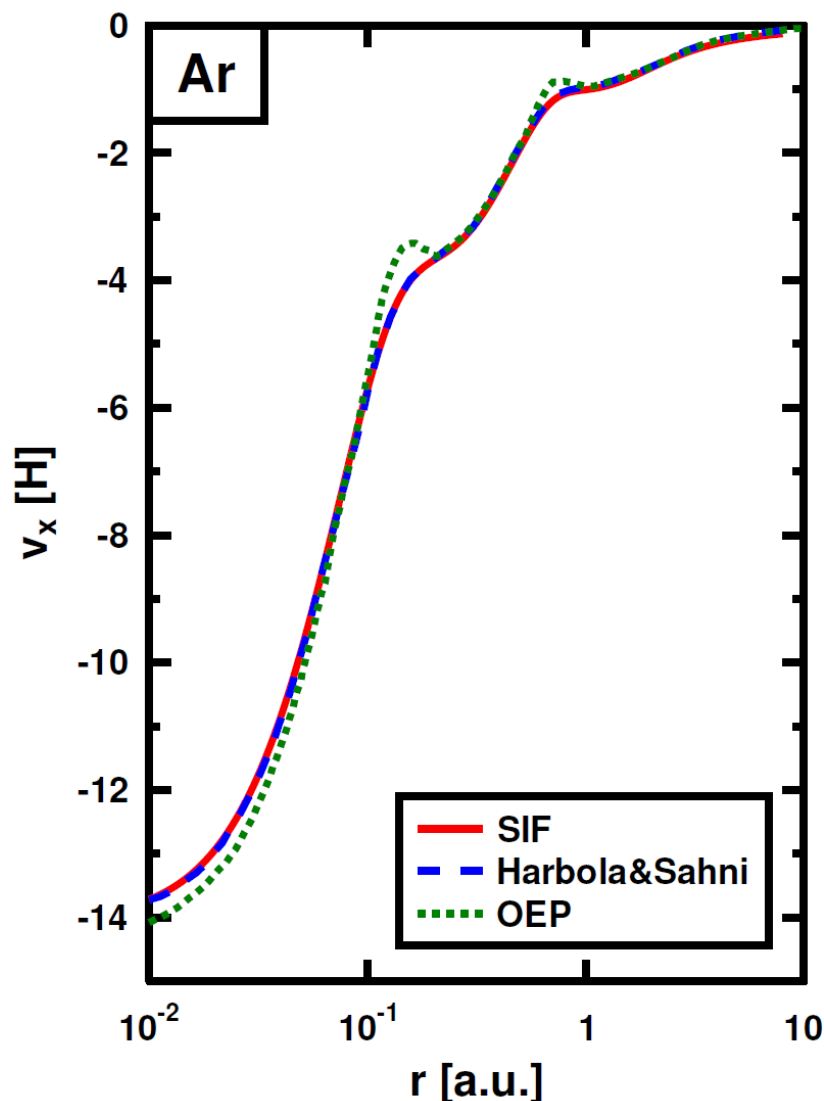
$$\frac{\delta E}{\delta n} = 0$$

OEP condition for the ground state:

$$0 = \frac{\delta E}{\delta v_s(\mathbf{r})} = \int d\mathbf{r}' \frac{\delta E}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})}$$

- The domain of search within the OEP is augmented compared to the DFT domain.

- This can lead to lower energies than DFT results.

Alternative Approach

M. K. Harbola and V. Sahni, Phys. Rev. Lett. **62**, 489 (1989)

using classical electrodynamics

$$E_x[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

corresponding electric field

$$\vec{E}_x = \int \frac{\rho_x(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'$$

The potential is the work bringing an electron from infinity to **r**:

$$W_x(\mathbf{r}) = -\int_{-\infty}^{\mathbf{r}} \vec{E}_x \cdot dl$$

Conjecture:

$$W_x(\mathbf{r}) = v_x(\mathbf{r})$$

Summary

- a solution to the self interaction problem (for non-periodic systems) was presented, using only derivatives with respect to the density

- analytic, closed form treatment of the Coulomb energy within Kohn-Sham density functional theory

- an explicit expression for calculating the Coulomb potential, avoiding self-interaction effects by construction

- quantum mechanically correct form of the Coulomb energy using the pair density

- fulfills the 2nd Hohenberg-Kohn theorem: no lower than ground state energy

- formalism and code is developed for all non-periodic systems (so far) (need: all occupied orbitals, boundary conditions for Poisson solver)

- further developments: periodic systems

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